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Optimized Microwave Digestion and Quantification Procedure for Boron Carbide samples

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A microwave-assisted HNO₃-H₂SO₄-HF digestion system was explored/optimized for the total dissolution of Boron Carbide samples followed by multi-elemental determination using ICP-MS and ICP-OES, in order to improve the methods used in a previous try using a microwave-assisted H₂O₂-HNO₃-HF digestion system.

The samples were microwave digested to accomplish complete dissolution needed to perform quantitative analysis of their metal content. Two Boron Carbide samples were provided to us: JM10 and JM11. The Boron Carbide samples were completely dissolved at the end of the optimized microwave digestion procedure that was developed. The digested samples were analyzed for metals mostly by ICP-MS; few elements were analyzed by ICP-OES.

Microwave digestion reactions were performed in a Titan MPS instrument (Perkin Elmer, USA). Titan MPS instrument is equipped with Temperature and Pressure regulations and controlled by software. Each microwave digestion batch contained the samples of interest along with a reagent blank and one certified standard (1632e) in order to (i) compensate for the contaminations present in the reagents, (ii) ensure that the digestion was complete and (iii) that there was a good recovery of all the constituents. The certified standard used (1632e) was provided with USGS certificates of analysis.

Description of the optimized microwave digestion methods

Approximately 0.03 g of each sample was weighted out and placed in separate reaction vessels. At the same time a standard 1632e sample was prepared by weighting out approximately 0.03 g of 1632e standard. All the weights for samples and 1632e standard were carefully recorded and used further in all the calculations. Also, a reagent blank sample was also prepared. Two methods were tested out for microwave digestion efficacy. The two Microwave methods differ by the volumes of reagents used.

All laboratory water used in this process was obtained using a MilliQ Integral 15 Water Purification System (Millipore Sigma, USA).

Method A. The following reagents were added to each vessel in this order: 5 mL Optima Nitric Acid (Trace Metal Grade, Thermo Fisher Scientific, NJ), 1 mL Optima Grade Hydrofluoric Acid (HF) (Thermo Fisher Scientific, NJ) and 1.5 mL Sulfuric Acid Trace metal grade (Fisher Chemicals, Canada)

Method B. The following reagents were added to the each of the vessel in this order: 1.5 mL Optima Nitric Acid (Trace Metal Grade, Thermo Fisher Scientific, NJ), 0.75 mL Optima Grade Hydrofluoric Acid (HF) (Thermo Fisher Scientific, NJ) and 1.5 mL Sulfuric Acid Trace metal grade (Fisher Chemicals, Canada).

After adding the reagents, the vessels were shaken carefully and were placed in the Titan MPS instrument. After that the microwave digestion process was started.

Same **Parameters** were used for the two microwave digestion methods as follows:

T (° C)	Hold (min)
150	10
190	15
220	30
50	5

The microwave digestion process involved 3 cycles of 85 minutes each. After the first cycle the microwave digestion samples were checked for solubilization. For the samples using the method A a complete solubilization was observed after the first cycle. For the samples using the method B, at the end of the first cycle not all the samples were completely solubilized. The vessels were placed carefully back into Titan MPS instrument and another cycle, using the same parameters, was started. At the end of the second cycle, after cooling down, the samples were checked for complete solubilization and a complete solubilization of all samples was achieved. Next, 8 mL of 4% Boric Acid (Sigma Aldrich, USA) were added to the each of the reaction vessels to neutralize the excess HF. An additional microwave digestion cycle, using the same parameters, was conducted. At the end of the third cycle, after cooling down, the digested samples were placed in Teflon containers for storage and subsequent quantification.

A picture of the digested samples in the Teflon containers is shown below.



The digested samples were analyzed using inductively coupled plasma mass spectrometry (ICP-MS) for trace metal, most of the major cations, other metal elements and Rare Earth Elements (REE) analysis and using inductively coupled plasma optical emission spectrometry (ICP-OES) for Si and K. New ICP-MS methods were developed for quantification of all the available metals. Please keep in mind that some metals were not analyzed at GGRL before, and needed a procedure development.

Trace metals, majority of the major cations, other elements and Rare Earth Elements concentrations were analyzed using a Perkin Elmer Nexion 300S ICP-MS following US EPA Method 200.8. The ICP-MS system was calibrated using external standards prepared using Indium (In) (Spex CertiPrep, Metuchen, NJ) as an internal standard. Ultra high-purity Optima Nitric Acid (Fisher Trace

Metal Grade) (Thermo Fisher Scientific, Fair Lawn, NJ) was added to samples, QC check standards and calibration standards. Internal standard In was spiked into samples and standards to correct for matrix effects. The calibration curve had an R² of 0.999 for each analyte. The recoveries were mostly in the 90-110% range. The samples were diluted prior to analysis in order to minimize matrix effects and to allow the analytes of interest to remain within the linear dynamic range of the calibrations. Two separate dilutions and a certified standard, NIST 1640a, (NIST, Gaithersburg, MD) were used in order to validate the ICP-MS runs and to provide the accuracy of the multi-element calibrations and quantifications. Reagent blanks were processed for background subtraction in order to subtract any contamination contributions from the use of trace metals grade reagents. Typical ICP-MS parameters were: 1600 W ICP RF power, 18 L/min plasma gas flow, 1.2 L/min auxiliary gas flow; 0.84 L/min nebulizer gas flow.

Major cation concentrations were analyzed by ICP-OES following US EPA Method 200.7. The ICP-OES instrument used was the Perkin Elmer Optima 2100 DV. The ICP-OES system was calibrated using external standards using Indium (In) (Spex CertiPrep, Metuchen, NJ) as an internal standard. Ultra high-purity Optima nitric acid (Fisher Trace Metal Grade) (Thermo Fisher Scientific, Fair Lawn, NJ) was used for digested samples, QC sample and standard preparation. Internal standard Indium (In) (Spex CertiPrep, Metuchen, NJ) was added to both samples and standards to correct for matrix effects. The calibration curve had an R² of 0.999 for each analyte. The recoveries were in the 90-110% range. The samples were diluted prior to analysis in order to minimize matrix effects and to allow the analytes of interest to remain within the linear dynamic range of the calibrations. Spex CertiPrep Instrument Calibration Standard, ICS 3 (Spex CertiPrep, Metuchen, NJ), was used as a check standard to provide the accuracy of the multi-element calibrations and quantifications. Reagent blanks were processed for background subtraction in order to subtract any contamination contributions from the use of trace metals grade reagents. Typical ICP-OES parameters were: 1300 W forward power, 15 L/min cooling gas flow, 0.2 L/min auxiliary gas flow, 0.8 L/min nebulizer gas flow and 1.5 mL/min sample uptake.

A total of 65 metals were quantified as follows: Ag, Al, As, Au, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Ga, Gd, Hf, Hg, Ho, Ir, K, La, Li, Lu, Mg, Mn, Mo, Na, Nb, Nd, Ni, Os, Pb, Pd, Pr, Pt, Rb, Re, Rh, Ru, Sb, Sc, Se, Si, Sm, Sn, Sr, Ta, Tb, Te, Th, Ti, Tl, Tm, U, V, W, Y, Yb, Zn and Zr.

Boron (B) was not analyzed- it is present in the matrix and, also, Boric Acid is used to neutralize the unreacted HF. In was used as an Internal Standard in quantification procedures. Because the certified standard 1632e was used as a sample in the microwave digestion process, had great recoveries and the recovered concentrations for it matched the concentrations disclosed in the USGS certificate of analysis our reported limits of detection for elements is really low, based on the recoveries obtained for the 1632e standard.

The attached file has our results compared to the EAG lab results. Where there are discrepancies between the two sets of concentrations, the samples were reanalyzed for the specific analytes and the same results, as our initial concentration, were obtained. Comparing the results it is apparent that the EAG reported concentrations for a both samples, JM10 and JM11, are lower for the following analytes Al, Ba, Ca, Co, Cr, Fe, Mn, Ni, Si, Ti, V, W than our reported concentrations. A possible explanation for this is that the EAG microwave digestion method is not complete, they do not use H₂SO₄ when performing the digestion. Previously, we used a similar digestion method with the method

that the EAG labs is using and we did not achieve complete dissolution during the microwave digestion process for the Boron Carbide samples.